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An updated Quantitative Water Air Sediment Interaction (QWASI) model for evaluating chemical fate and input parameter sensitivities in aquatic systems: Application to D5 (decamethylcyclopentasiloxane) and PCB-180 in two lakes

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HIGHLIGHTS

- The QWASI model is a fugacity-based mass balance chemical fate model.
- The model was reformatted to encourage "Good Modeling Practices".
- The model was revised in spreadsheet format to accommodate sensitivity analysis.
- The model is illustratively applied to two chemicals in two lakes.
- Two strategies for assessing uncertainty are discussed.

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ABSTRACT

The QWASI fugacity mass balance model has been widely used since 1983 for both scientific and regulatory purposes to estimate the concentrations of organic chemicals in water and sediment, given an assumed rate of chemical emission, advective inflow in water or deposition from the atmosphere. It has become apparent that an updated version is required, especially to incorporate improved methods of obtaining input parameters such as partition coefficients. Accordingly, the model has been revised and it is now available in spreadsheet format. Changes to the model are described and the new version is applied to two chemicals, D5 (decamethylcyclopentasiloxane) and PCB-180, in two lakes, Lake Pepin (MN, USA) and Lake Ontario, showing the model's capability of illustrating both the chemical to chemical differences and lake to lake differences. Since there are now increased regulatory demands for rigorous sensitivity and uncertainty analyses, these aspects are discussed and two approaches are illustrated. It is concluded that the new QWASI water quality model can be of value for both evaluative and simulation purposes, thus providing a tool for obtaining an improved understanding of chemical mass balances in lakes, as a contribution to the assessment of fate and exposure and as a step towards the assessment of risk.

1. Introduction

In 1983 a set of two papers was published describing simple models of chemical fate in lakes and rivers (Mackay et al., 1983a, 1983b), namely the QWASI (Quantitative Water Air Sediment Interaction) models. The models were compiled using the fugacity concept and have been made freely available as software from the website of the Canadian Centre for Environmental Modelling and Chemistry (CEMC) and have been widely applied to specific environmental systems (e.g. Mackay, 1989). The QWASI lake model addressed here treats a well-mixed water body and includes the processes depicted in the mass balance figures presented later. Chemical inputs are by direct emissions, advective inflows of water and suspended particles, and deposition from an atmospheric compartment with a defined concentration by wet and dry aerosol and gaseous deposition. Steady state mass balance equations are compiled separately for the water and sediment compartments with chemical masses and concentrations expressed as fugacities in water and in sediment. Although the model simulates a steady

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state condition it can be adapted to treat dynamic conditions as a pair of first order differential equations that can be solved analytically or numerically. The equations are readily interpretable because all process rates are expressed as products of the fugacity in the source phase and a D value which can represent reactions, diffusion or advective transport. Full details of the equations and assumptions are given in the original papers and in the text by Mackay (2001). The simplicity of the equations has facilitated the extension of both the lake and river models to treat more complex multi-compartment systems such as segmented lakes (Ling et al., 1993; Diamond et al., 1994, 1996; Mackay and Hickie, 2000) or they can be set up as a number of well mixed connected river reaches (Warren et al., 2005, 2007; Ethier et al., 2008). Insights into the time response of the system can be obtained by examining the residence times of the chemical in each compartment.

In a recent paper (Hughes et al., 2012) we described an updated state of the science EQuilibrium Criterion (EQC) model that is used to provide a screening level evaluation of the likely fate of a chemical that is introduced into a multi-media environment by various modes of entry. This evaluation can then be followed by a more detailed system-specific evaluation such as the QWASI model. This EQC screening level approach was described for the volatile permethyl siloxane D5 (decamethylcyclopentasiloxane, CAS No 541-02-6). In this paper we illustrate this type of evaluation by application of an updated state of the science QWASI model to D5 and PCB-180 (2,2′,3,4,4′,5,5′-heptachlorobiphenyl, CAS No 35065-29-3) for two aquatic receiving environments, namely Lake Pepin (MN, USA) and Lake Ontario. Whelan (2013) has recently reported a similar evaluation using a custom-modified QWASI model and illustrated the importance of determining parameter sensitivities. In the present study we expand on these simulations using the new QWASI Lake model. Finally, we outline and illustrate strategies for determining and displaying a comprehensive analysis of the sensitivities of the results to each input parameter and uncertainties in the key output parameters.

2. Application of the model

If an estimated or measured discharge rate of a chemical into a specific water body is available, for example from a Waste Water Treatment Plant (WWTP), the model can translate this rate into estimated steady state concentrations. These concentrations can be used for screening level assessments of fate and exposure, and can be compared with monitoring data to investigate whether the fate processes are being reliably simulated. The model also estimates the absolute and relative quantities of the chemical and its corresponding residence times in water, suspended particles, sediments and in the system as a whole. This can help guide monitoring efforts and provides insights into the likely response times of the compartments to changes in emission rates, for example, remediation following a reduction or cessation of discharges.

Rates of key transport processes are estimated, thus the relative importance of competing loss processes such as degrading reactions, volatilization, advective outflow and sedimentation can be ascertained. This can identify the key transport and transformation rate parameters and justify efforts to obtain more accurate values.

Finally, by using fugacity, the relative equilibrium status of compartments becomes obvious. An example is air–water exchange in which the net driving force for diffusion can be from water to air or air to water depending on local conditions. A simple direct estimate can be made of equilibrium concentrations in biota resident in water and sediment by assuming equi-fugacity to deduce equilibrium concentrations in organism lipids. These simple estimates can justify the application of more detailed bioaccumulation and food web models such as that of Arnot and Gobas (2004).

It can be argued that the fate of a chemical in an aquatic system is not fully understood until a full mass balance accounting is obtained. The QWASI model can achieve this goal.

3. Specific changes to the model

Feedback from users of the model for the above purposes indicates a need for an updated version that better meets current scientific and regulatory needs. First, although the software version has proved to be reliable and easy to use, there has been an expressed need for a version that is based on a Microsoft Excel spreadsheet platform. The use of this spreadsheet makes the model more readily available to potential users and sensitivity and uncertainty analyses are more readily conducted. This latter aspect has proved to be particularly important from a regulatory perspective by enabling the user to identify the more sensitive parameters and explore the implications of variations in input parameter values. The use of this platform facilitates linking it to other spreadsheet models that may address the efficiency in WWTPs, run-off from soils and bioaccumulation in organisms or food webs. Accordingly, the new model is compiled as an Excel spreadsheet and, as with the previous version, it is freely available from the Trent University CEMC web site (www.trentu.ca/cemc).

Second, in the original model partition coefficients were calculated from solubility, vapor pressure and octanol water partition coefficient (K_{OW}), the last of which was used to estimate partitioning to organic carbon in sediments and particles as K_{OC}. Modern regulations often require empirical rather than estimated values derived from simple K_{OW}–K_{OC} quantitative structure–activity relationships (QSARs). More sophisticated methods are now available to calculate partition coefficients such as using Linear Free Energy relationships as reviewed by Endo et al. (2013) and quantum chemical programs such as SPARC (Hilal et al., 2003) and COSMOtherm (Klamt, 2005). In the new version all partition coefficients are input directly. Guidance is provided in a worksheet on the likely magnitude of certain values and their temperature dependence.

Third, all input data are summarized in three worksheets and space is provided to document the data sources and perceived accuracy of all input values. Notes and comments can be included. Such information is invaluable when the model output is examined by another party, for example during regulatory proceedings. This approach is in accord with the principles of Good Modeling Practice described by Buser et al. (2012).

4. Application of the model to D5 and PCB-180

The updated QWASI model is applied here for illustrative purposes to two chemicals, D5 and PCB-180 in two lakes, Lake Pepin, which is a natural lake on the Mississippi River located approximately 80 km downstream of Minneapolis and Saint Paul, and Lake Ontario. These lakes differ greatly in size, depth, trophic status, and hydraulic retention time, Lake Pepin being some 12 d and Lake Ontario some 7 years. The properties of the chemicals and lakes are given in Table 1. The assumed temperature was 9 °C in Lake Ontario and 14 °C in Lake Pepin as suggested by Whelan (2013). Illustrative emission rates of 100 kg year^{-1} of the chemicals are assumed for both lakes. It is emphasized that these rates are entirely hypothetical, the aim being to evaluate and compare both the relative fates of the two chemicals, behaviors in small and large lakes and display the model's capabilities.

Although it is subject to thermal stratification, Lake Pepin has a relatively low volume and short retention time and can probably